Pakistan Journal of Marine Sciences, Vol. 17(1), 1-11, 2008

DETERMINATION OF SOME METAL IONS IN AQUATIC ENVIRONS BY ATOMIC ABSORPTION SPECTROMETRY AFTER CONCENTRATION WITH MODIFIED SILICA

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ABSTRACT: The uptake behaviour of porous silica modified with N-propylsalicylaldimine (IE11) and Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) metal ions were studied. The Log k_d values were found to be within the range 2.19 - 5.16 depending on pH and time of stirring. IE11 was used in the separation and preconcentration of Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) from some natural water samples. The data were compared with those obtained by the solvent extraction method (APDC/MIBK). The proposed methodology permits verification of improvements in the water quality of the Nile River, probably attributed to moderately high floods of the last few years. The method was found to be accurate and precise and not subject to random error.

KEYWORDS: Atomic Absorption, heavy metal, Spectrometry ions, modified silica, natural waters.

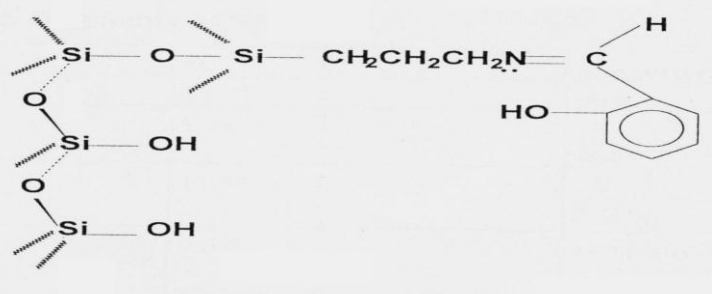
INTRODUCTION

Within recent years, solvent extraction and coprecipitation have been increasingly replaced by sorbent (solid phase) extraction and ion exchange. The markedly lower quantity of reagents required is frequently cited as an advantage, although that is strongly method-dependent. A further advantage is that the solid phase can be repeatedly used.

Sorption and ion exchange have been extensively studied for different analytical applications (Kenawy *et al.,* 1993, 2000). Some natural and synthetic materials such as silica, carbon, cellulose and synthetic polymers have been used either unmodified or after modification by physical or chemical treatments. In the last two decades, the use of silica-based ion exchangers in preconcentration and separation of trace heavy metal ions from different media has been of particular interest. Advantages of silica as a base for chelating agents to be used as ion exchangers, over the organic polymers, are its good mechanical and thermal stability. It is also less susceptible to swelling, shrinking and microbial and radiation decay (Leyden and Luttrell, 1975).

The use of chelating agents is a promising route for the activation of the surface of the silica to raise its efficiency and selectivity of extraction. The following agents were used to separate trace amounts of heavy metal ions from their parent solutions: 3-aminopropyltriethoxysilane, propanethiol modified silica gel (Abou EI-Sherbini *et al.,* 2003a), mono- and bis-salicylaldehyde and naphthaldehyde Schiff's bases based on silica gel (Soliman *et al.,* 2001), hexathia-18-crown-6-tetraone based on octadecyl silica membrane disc (Yamini *et al.,* 1997) and 8-hydroxyquinoline immobilized on fluorinated metal alkoxide glass (MAF -8HQ) (Sohrin *et al.,* 1998). It was found that the efficiency of the separation depends on the concentration of the metal ion, the nature of the extractant and its surface area, temperature and the stability of the formed chelate.

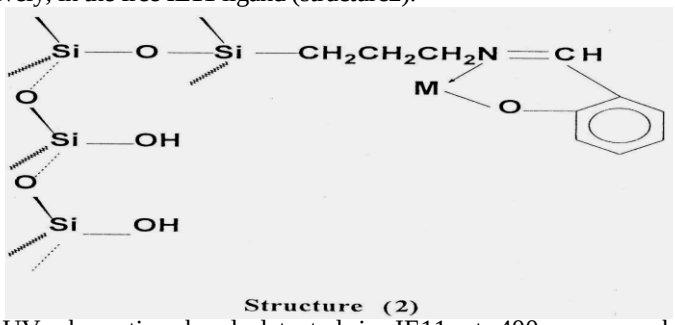
The synthesis and characterization of controlled pore silica modified with N-propylsalicylaldimine was reported by Abou El- Sherbini *et al.,* (2003a). B/Si ratio of 6.5/1 in borosilicate glass was effective in obtaining highly porous silica by acid leaching that led to high exchange capacity (C_{IE11} = 0.36 mmole Cu/g, pH = 5.5) in the obtained ion exchanger (IE11, structure 1).



Structure (1)

The complexation behavior of IE11 with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+} and UO_2^{2+} was investigated and confirmed by electronic and infrared spectra and electrical properties (Abou El-Sherbini *et al.,* 2003b).

IR and UV spectra of IE11 and its complexes with Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) revealed that the bonding between these metal ions and the N-propylsalicylaldimine substrate was attributed to complexation through O and N. This was concluded from the disappearance of the IR bands at 1276 and 1492 cm^{-1} in the spectra of the complexes assigned to δ(O-H) $_{in\ plane}$ and δ (N-H)$_{in\ plane}$, respectively, in the free IE11 ligand (structure2).



Structure (2)

Also, the UV absorption band detected in IE11 at 400 nm was blue shifted on complexation. The stochiometry of the resulting solid complexation. The stochiometry of the resulting solid complex preferred to be 1:1 (N-porpylsalicylaldimine-M). This may be due to the steric hindrance of silica moiety and completed the coordination with two molecules of water (Abou-El-Sherbini *et al.,* 2003 b).

The aim of the present paper is to study the uptake behavior of IE11 towards Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) to suggest the optimum conditions for the separation, preconcentration and elution of these metal ions from aquatic environments.

MATERIALS AND METHODS

Atomic absorption spectrometry (AAS): Analysis of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) was performed using the Perkin Elmer 2380 flame atomic absorption spectrophotometer.

Infrared spectra: Infrared reflectance spectra were recorded on a Bruker IFS 48 FTIR spectrometer using a gold ball as a reference. This measurement was performed in Physikalisch Technische Bundesanstalt Braunschweig, Germany.

Electronic spectra: UV absorption spectrometric measurements were, performed using an UNICAM UV- Vis uvz spectrometer. The sample was introduced as slurry with nujol on a Whatmann filter paper strip using another one wetted with nujol as a blank. (Abou El-Sherbini *et al.,* 2003b).

Adjustment of pH and pH-metric titration: The pH of each sample solution was adjusted within the range of 3 to 11.5 using a Beckman (Fullerton, CA) digital pH meter with glass and saturated calomel electrodes calibrated on the operation state using standard buffer solutions at 25^{o}C.

Preparation of porous silica modified with N-propylsalicylaldimine (IE11) and its complexes with Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II): Porous silica (PS) was prepared by acid leaching of sieved borosilicate glass (<70 µm, B/Si = 6.5:1) obtained by sol-gel technique (Soliman, *et al.,* 2001). The grafting with 3-aminopropyltrimethoxysilane (APMS) was achieved by refluxing 18 g PS with 36 mL APMS in xylene at 80^{o}C for 24 h. 11 g of the yield was washed with ethyl alcohol and refluxed with 15 mL salicylaldehyde in 50 mL dimethyl sulfoxide (DMSO) at 90^{o} C for 24 h. The obtained ion-exchange (yellow) was washed with EtOH and dried at 80^{o}C (Abou El-Sherbini *et al.,* 2003a).

Batch procedure: The data are given as the simple mean of three replicates whereas those of application were repeated five times from which the statistical evaluation was performed. A total of 20 mg of IE11 was suspended with constant stirring for 30 min in 25 mL of 10 µg/mL of Cd (II), Cr (III), Cu (II), Mn (II) or Pb (II) at the desired pH value in the range of 3-11.5. The concentrations of the investigated ions in the filtrates were determined by AAS. The distribution coefficient (K_d) was determined using the equation.

$$K_d = \frac{C_{i.ex}\,(\mu g/g)}{C_{sol}\,(\mu g/mL)} \quad mL/g$$

Where $C_{i.ex}$ is the metal concentration in the ion exchanger (solid phase) and C_{sol} is the metal ion concentration in the solution phase.

The study of the separation of Cr^{3+} and Mn^{2+}, obtained by the reduction of CrO_4^{2-} and MnO_4^- respectively, was carried out. The reduction was performed by shaking with 0.5 mL H_2O_2 (30% wt/vol) for 5 min after acidification with H_2SO_4. Excess H_2O_2 was expelled by heating for 15 min at 90^{o}C, then the separation process was performed as indicated above.
The optimum conditions (pH = 9.0 - 9.5, time of stirring = 30 min and weight of IE11 = 100 mg) were applied during the study of the interfering effects of different foreign ions on the efficiency of separation. The same conditions were also used in the study of the effect of concentration of the eluent acids (10 mL of HCl or HNO_3) on the recovery.

Sampling: Surface water samples were collected on 20 Nov. 2003, from the Nile River (at - Mansoura, Faraskor, Damietta, Gerbi and Ras Elbar), the Mediterranean Sea (at Ras Elbar and Damietta Port), El-Manzalah Lake, the Suez Gulf and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and suspended matter was determined. The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg $CaCO_3$/L were determined according to the methods outlined by Strickland and Parsons (1968). The samples were then acidified with concentrated HNO_3 to pH $\cong$ 2 and preserved in polyethylene vessels.

The organic matter was digested prior to the separation process; 0.5 g of $K_2S_2O_8$ and 5 mL of 98 % (wt/vol) H_2SO_4 were added to 1 L of the water sample and heated for 30 min at 95^{o} C. After cooling to room temperature, 100 mg of IE11 was added to the sample and the pH value was adjusted to 9.0-9.5 and stirred for 30 min, then filtered. 50 mg of the ion exchanger was added to the filtrate, the pH value was controlled and the sample was stirred again for 30 min and filtered. Both residues were gathered and the collected metal ions were released by 10 mL 2M HNO_3, to give a concentration factor of 100 fold.

The concentration of dissolved Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) were determined in water by solvent extraction using ammonium pyrolidine dithiocarbamate (APDC) and methyl isobutylketone (MIBK) as a standard method (APHA, 1989).

RESULTS AND DISCUSSION

Uptake behaviour of IE11

Effect of pH: Figure 1 presents the effect of pH on the up take behaviour of Cd (II), Cr (III), Cu (III), Mn (II) and Pb (II) on IE11. At low pH, the distribution coefficients were generally low for all the five analytes, which is attributed to the incomplete ionization of the ionogenic group of the ion exchanger. The distribution coefficient of the metal ions on IE11 increased with pH and reached its maximum at pH $\cong$ 9.0 but decreased in cases of Cr^{3+} and Pb^{2+} probably due to the formation of the anionic ions CrO_2^- and PbO_2^{2-} respectively. The $LogK_d$ values at pH = 9.0-9.5 were 4.68, 5.16, 4.83, 5.09, 4.70 for Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) respectively.

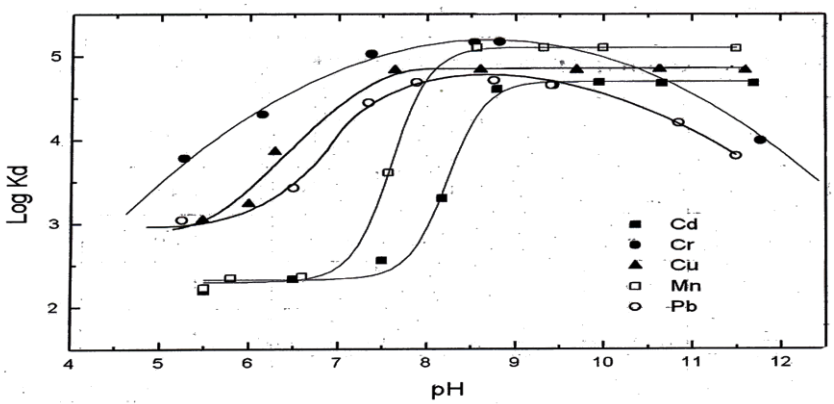


Fig.1. Effect of pH on the distribution coefficient of Cr (III), Mn (II), Cu (II), Cd (II) and Pb (II) on IEE11.

Effect of time of stirring, concentration of eluent acids and some interfering species: Figure 2 presents the effect of time of stirring on the recovery of the investigated metal ions at pH = 9.0-9.5 using IE11. The ion exchanger showed fast kinetics of equilibration. Fig. 2 shows that the recovery of metal ions under investigation took placed in the range of 60 - 100% recovery after 1 min. This indicates that the reaction between solid-phase IE11 and metal ions is fast, while the concentration of metal ion in water is very low. Consequently a long time is needed for equilibration thirty minutes of stirring was satisfactory to reach maximum values of recovery (Kenawy, *et al.* 2000).

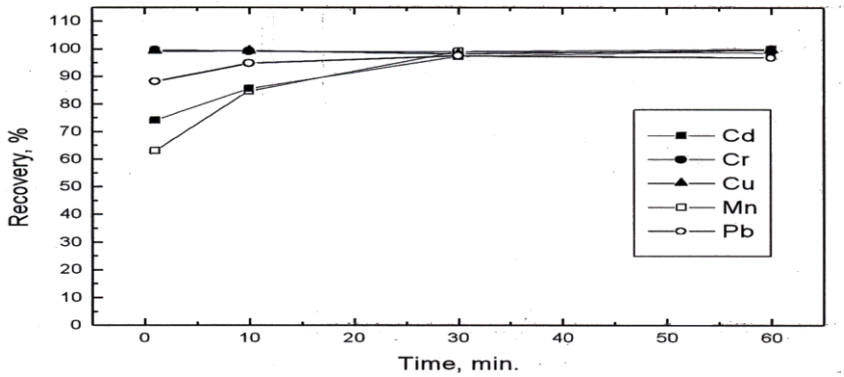


Fig. 2. Effect of time of stirring on the recovery of Cr (III), Mn (II), Cu (II), Cd (II) and Pb (II) separated on 20mg IE11 at pH = 9.0-9.5.

Figure 3 (A & B) shows the effect of concentration of eluting acids on the recovery after separation at pH 9.0-9.5 and weight = 100 mg. HCl showed relatively better leaching efficiency of the metal ions from the ion exchanger than HNO_3 except in case of Cu^{2+} where the recovery was lower with HCl. This may be attributed to the formation of anionic chloro-complex with Cu^{2+} that may be bounded to the protonated imine nitrogen of the substrate at pH < 4 (Abou El-Sherbini *et al.,* 2003a). Molar concentrations of HCl and HNO_3 were sufficient to obtain maximum recovery, but the latter is recommended for application due to the limitation of using HCl in case of Pb^{2+}. However, the eluting efficiency of CMPS-PAN resin (Kenawy *et al.,* 2000), is small accompanied with that strong chelation between the ion exchanger and the metal ions not favoured, due to irreversible binding (Leyden and Luttrell, 1975).

No effect on the recovery of the investigated metal ions was found from acetate, oxalate (200 mg/L), nitrate, sulfate, phosphate, NH_4^+, Mg^{2+} and Ca^{2+} (1000 mg/L) ions. Citrate and EDTA (200 mg/L) showed strong interfering effect on the recovery of the investigated metal ions (R = 6.4 -94.2%) due to the formation of complexes with the metal ions of higher stability than those with IE11. Consequently, the organic matter present in the natural water samples (which may have the same effect) should first be digested prior to the application process.

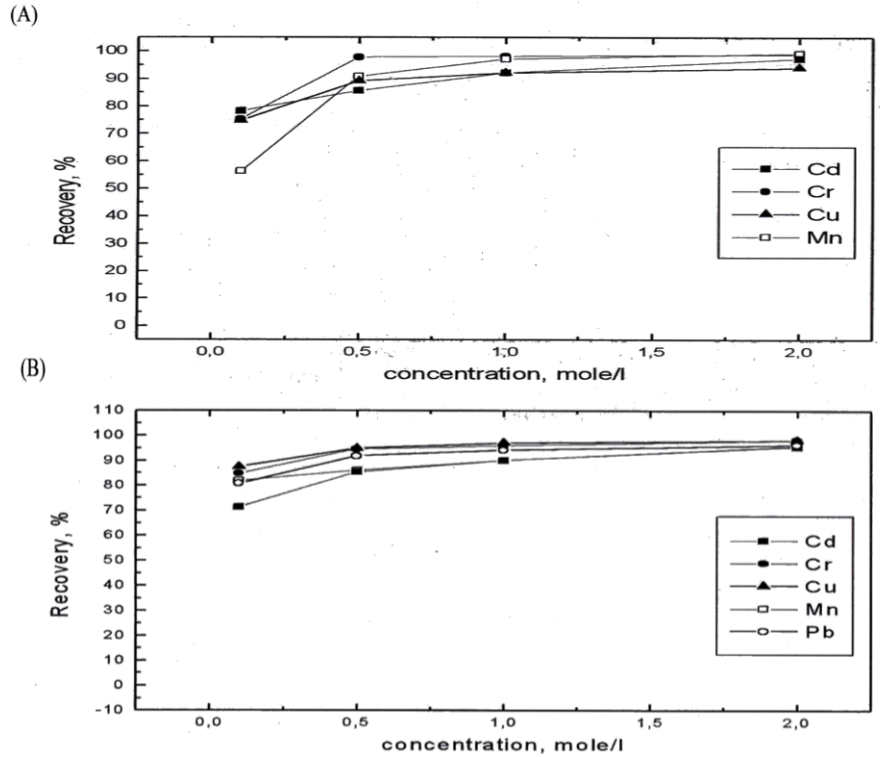


Fig.3. Effect oh HCI (A) HNO_3 (B) concentration on the recovery of Cr (III), Mn, Cu (II),Cd (II) and Pb (II) separated on 20 mg IE11 at pH = 9.0-9.5 and time of stirring = 30 min.

Separation of Cr (III) and Mn (II) obtained from chromate and permanganate: The separation of Cr (III) and Mn (II) obtained by reduction of their higher oxidation states from chromate (Cr (VI)) and permanganate (Mn (VIl)), respectively, using H_2O_2 in acidic medium led to a recovery of 94.5 and 98.5 %, respectively. This is slightly lower than the values obtained without previous reduction (99.1 and 99.0 % respectively) indicating the effectiveness of the reduction process.

Nature of bonding between metal ions and IE11: The pH-metric titration of the free silica-based N-propylsalicylaldimine ion exchanger, showed the presence of two inflections attributed to neutralization of the proton gained to the imine nitrogen (acidic range) and another from the phenolic group (basic range) (Abou El-Sherbini *et al.,* 2003a), (Fig 4). The second inflection in the free IE11 at pH = 9.7, was shifted to lower pH values and decrease in the sequences Cr (III) > Cu (II) > Pb (II) > Mn (II) > Cd (II), i.e. decreasing complex strength.

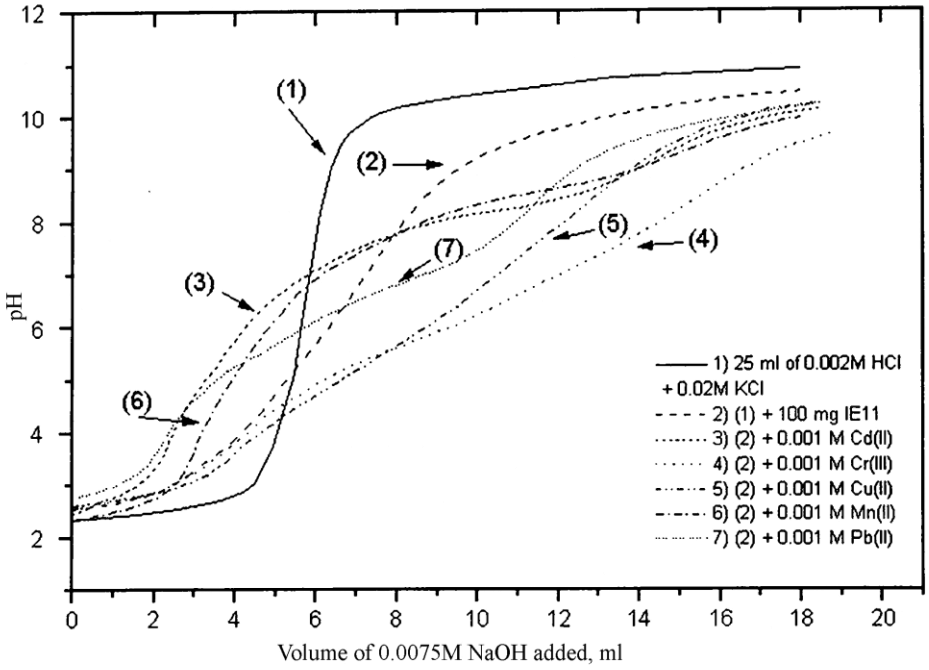


Fig.4. The pH-metric titration curves of IE11, its complexes with Cr, (III), Mn (II), Cu (II), Cd (II) and Pb (II).

Analytical application

Water quality measurements: The pH of the water samples was on the alkaline sides and ranged between 8.25 at Suez Gulf and 7.70 at Ras Elbar (brackish water). TDS determined for the water samples indicated that only samples collected from the Nile River at Mansoura and Faraskor could be considered fresh water (Abdallah *et al.* 1999) while those from River at Damietta Bridge, Gerbi and Ras Elbar, seawater at Datnietta Port and EI-Manzalah Lake were brackish water (Hamed and Said, 2000). Water samples from Ras Elbar, Port Said and Suez Gulf were saline (Hamed, 1996). It is noteworthy to mention that the relative low TDS in seawater taken from Damietta Port may be attributed to the fresh water effluent from a small canal. TSM of the Nile River and tap water was found to be low varying within the range from 0.075 to 0.159 g/L. DO varied from 3.54 mg O_2 / L at El-Manzalah to 6.94 mg O_2/L at Ras Elbar. The minimum value of DO at El-Manzalah could probably be due to the effect of the disposal of domestic wastewater (Meshal, 1967). Alkalinity of the surface water varied from 138.0 to 176.5 mg $CaCO_3$/L at Ras Elbar sea and El-Manzalah Lake waters, respectively. The high alkalinity value at El-Manzalah was essentially because of the disposal of sewage with other domestic effluents in EI-Manzalah Lake. The data of water quality measurements are presented in Table 1.

Table 1. Water quality measurements of the water samples collected from different locations on 20 Nov, 2003.

Parameters (Location)	pH	TDS (g/L)	TSM (g/L)	DO (mg O_2 /L)	Alkalinity (mg $CaCO_3$/L)
Mansoura (river water)	7.9	0.506	0.075	4.10	145.0
Faraskor (river water)	8.08	0.988	0.101	6.60	147.5
Damietta Bridge (brackish water)	7.6	2.086	0.122	6.43	157.0
Gerbi (brackish water)	7.87	3.090	0.106	4.49	153.5
Ras-Elbar (brackish water)	7.70	6.994	0.159	6.49	156.0
Ras-Elbar (seawater)	8.10	40.604	0.755	6.15	138.0
DamiettaPort (brackish water)	8.13	20.400	0.299	6.83	148.5
Port Said (seawater)	8.16	43.120	0.245	5.92	138.0
Suez Gulf (seawater)	8.25	47.804	0.299	6.03	148.5
EI-Manzalah (brackish water)	8.12	30.376	0.630	3.64	176.5
Mansoura city (tap water)	7.85	0.316	0.170	6.37	145.0

Water analysis: The ion exchange method was applied for the preconcentration and separation of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) in the water samples whereas solvent if extraction was used to evaluate the reliability of the ion exchange method, (Table 2). Suez Gulf showed generally low concentrations of heavy metal ions and the lowest values for the investigated metal ions. These values are in agreement with those recorded in Suez Gulf with the APDC/MIBK system (Abou El-Sherbini and Hamed, 2000). Generally, the concentrations of heavy metal ions increased in the region beginning from Damietta Bridge to the river effluent at Ras Elbar. The nearby locations showed higher concentrations of the investigated metal ions, which may be attributed to the domestic and anthropogenic activities along the side of the river in this region. However, these results are within the permissible levels and in agreement with those reported by Kenawy *et al.*, 2000; and Fifield and Haines, 2000.

The decrease in the heavy metal concentration compared to the reported values within the last thirteen years (El-Defrawy *et al.*, 1992; Kenawy *et al.*, 1993) could be due to the high to moderate flooding to the Nile River in 1998-2000 (Hafez *et al.*, 2001). These led to reclamation and improvements in the quality of water.

Comparison between the accuracy and precession of the present method with the reference solvent extraction APDC/MIBK method: The reliability of the ion exchange method was statistically examined for the analysis of Cd (II) and Pb (II), Tables 3 and 4 respectively, compared with the standard method of solvent extraction, based on the null hypothesis of $|t|_2$ for P=0.05and n= 10 (Miller and Miller, 1986).

Table 2. Multi-elements analysis of natural water samples using AAS for determination of some heavy metal preconcentration with solvent extraction (SE) (APDC/MIBK), and ion exchange separation by IE11. Io 9.0-9.5, weight of IE11 = 150mg, stirring time = 30 min at 25° C, x± ts n for n = 5, where X is the average equals 2057 for P = 0.05 and s it the standard deviation. The samples were collected at 20 Nov, 2003.

Location	Element							
	Cd (II)		Cr (III)		Cr (VI)	Cu (II)		Mn (II)
	SE	IE 11	SE	IE11	IE11	SE	IE11	SE
Mansoura (river water)	0.07±0.01	0.08±0.01	0.51±0.03	0.50±0.03	3.83±0.34	2.50±0.04	2.07±0.03	2.50±0.07
	0.02 [8], 0.2-2.3 [6]		1.0[8], 0.19-25.8[12]		0.75-7.29 [12]	5.0[8], 3-30[6]		7.0[8], 8.0-9
Faraskor (river water)	0.61±0.05	0.59±0.07	0.46±0.05	0.47±0.05	2.90±0.19	2.00±0.06	1.90±0.04	1.26±0.05
	0.02[8], 0.2-2.3[6]		1.0[8], 0.1925.8[12]		0.75-7.29[12]	5.0[8], 3-30[6]		7.0[8],8.0-9
Damietta Bridge (brackish water)	0.65±0.06	0.66±0.07	1.58±0.05	1.56±0.05	1.81±0.12	3.22±0.52	3.37±0.34	11.32±0.46
					0.75-7.29[12]			
Gerbi (brackish water)	1.44±0.03	1.46±0.04	2.60±0.07	2.62±0.07	3.28±0.28	3.00±0.07	3.05±0.07	3.11±0.55
					0.75-7.29			
Ras-Elbar (brackish water)	0.62±0.05	0.63±0.05	2.02±0.05	1.99±0.05	4.01±0.42	1.58±0.05	1.65±0.04	
					0.75-7.29[12]			
Ras-Elbar (seawater)	3.4±0.14	3.45±0.17	2.74±0.06	2.77±0.06	2.32±0.17	4.28±0.48	4.10±045	4.50±0.35
	0.1[5], 3.2-4.3[6]		0.05[8],0.02-0.18[12]		.48[17] 0.15-0.3[14	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1
Damietta Port (brackish water)	1.19±0.06	1.20±0.06	0.29±0.02	3.98±0.41	1.60±0.05	1.16±0.05	1.61±0.06	2.15±0.28
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		.48[14] 0.15-0.3[17	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1
Port Said (seawater)	0.69±0.05	0.70±0.05	1.50±0.05	1.47±0.05	2.24±0.17	2.32±0.07	2.31±0.07	2.56±0.15
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		.48[14] 0.15-0.3[17	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1
Suez Gulf (seawater)	0.25±0.01	0.26±0.01	0.06±0.01	0.07±0.01	2.53±0.19	0.20±0.01	0.19±0.01	0.26±0.05
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		48[14], 0.15-0.3[1]	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1
El-Manzalah (brackish water)	0.58±0.01	0.58±0.01	1.30±0.05	1.29±0.05	2.15±0.18	2.05±0.04	2.12±0.03	1.18±0.10
Mansoura city (tapwater)	0.58±0.05	0.62±0.07	0.42±0.03	0.41±0.03	2.62±0.24	1.01±0.04	1.04±0.03	1.03±0.06
	0.02[8], 0.2-10[6]		1.0[8], 0.15-50[12]		50[7]	3.0[8], 3.3-5.0[6]		10.0[8], 3.2-1

Mn (VII) was not detected in all samples, NB [No.] = number of reference alphabetically.

It was found that $|t|_2$ =0.00-2.3 for all the five metal ions that were less than the tabulated values ($|t|_2$ =2.3l) (Miller and Miller, 1986) with the exception of Cu (II) at Faraskor, Ras Elbar (brackish water) and El-Manzalah and Mn (II) at Damietta Port. No significant difference was found between the data obtained by the ion exchange and the solvent extraction methods. The precession and the random errors of the two sets of data (Tables 3 and 4) were deduced using the two-tailed F -test (Miller and Miller, 1986). It is clear that all the experimental $F_{4,4}$ values are between 1.00 and 2.54, less than the tabulated value of $F_{4,4}$ for p0.05 and n=10 (9.6) (Fifield and Haines, 2000). So, no significant difference between the two standard deviations at P=0.05 for both methods and the results obtained by both methods are not subjected to random errors (i.e. precise).

Table 3. Statistical evaluation for Cd (II) analysis in natural water samples after preconcentration by solvent extraction (method (1)) and ion exchanger (method (2)), n = 5.

Sample (Location)	Method (1)		Method (2)		S_p	$\|t\|_2$	Tow-tailed F-test
	X_1 Ng/mL	S_1	X_2 Ng//mL	S_2			
Tap water (Mansoura city)	0.58	0.050	0.62	0.060	0.06	1.15	1.44
Seawater (Ras-EIBar)	3.41	0.120	3.45	0.150	0.14	0.47	1.56
River water (Faraskour)	0.61	0.050	0.59	0.060	0.06	0.57	1.44
River water (Mansoura)	0.07	0.010	0.08	0.010	0.01	1.58	1.00
River water (Gerbi)	1.44	0.027	1.46	0.031	0.03	1.09	1.32

Table 4. Statistical evaluation for Pb (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and ion exchanger (method 2), n=5.

Sample (Location)	Method (1)		Method (2)		S_p	$\|t\|_2$	Two-tailed F-test
	X_1 ng/ml	S_1	X_2 ng/ml	S_2			
Tap water (Mansoura city)	1.50	0.069	1.53	0.072	0.071	0.70	1.09
Seawater (Ras-EIBar)	10.29	0.450	10.38	0.500	0.48	0.30	1.23
River water (Faraskour)	2.90	0.080	2.92	0.070	0.075	0.42	1.21
River water (Mansoura)	3.86	0.089	3.95	0.081	0.085	1.67	1.21
River water (Damietta)	4.15	0.071	4.18	0.068	0.07	0.70	1.09

Conclusion

The optimum conditions for separation of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) using N-propylsalicylaldimine based on porous silica were found to be pH = 9.0-9.5, time of stirring = ≥30 min. A concentration of 2M HNO_3 as an eluent was sufficient to obtain maximum recovery, 95.5, 98.1, 98.1, 95.7, 96.2% for Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II). In case of HCl, the recovery values were 97.2, 98.7, 93.9 and 99.0% for Cd (II), Cr (III), Cu (II) and Mn (II), respectively.

Citrate and EDTA showed interference to the separation of different metal ions, therefore, it was necessary to digest organic matter in natural samples before application. The separation of Cr (III) and Mn (II) obtained by reduction of their higher oxidation state forms, e.g., chromate and permanganate, using H_2O_2 in acidic medium, gave recoveries of 94.5 and 98.5 %, respectively.

The ion exchange method was applied for preconcentration and separation of Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) in the water samples in comparison with the standard solvent extraction method. The concentration of heavy metal ions increased obviously in the region beginning from Damietta Bridge to the river effluent at Ras Elbar, probably because of the domestic and anthropogenic activities along the side of the river in that region. Although the result are within the permissible level, an obvious decrease in the heavy metals concentration was observed compared with those reported at the early 1990's. This was explained in view of the numerous floods in the last few years that led to reclamation and improvement of the water quality of the Nile River.

The reliability of the ion exchange method was statistically examined compared with the standard method of solvent extraction. Testing of the experimental means and the standard deviations for the two methods using the null hypothesis of $| t |_2$ and the two tailed F-test respectively, for p=0.05 and n=10, indicated that the ion exchange method was accurate and precise.

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(Received on 23rd June, 2006)